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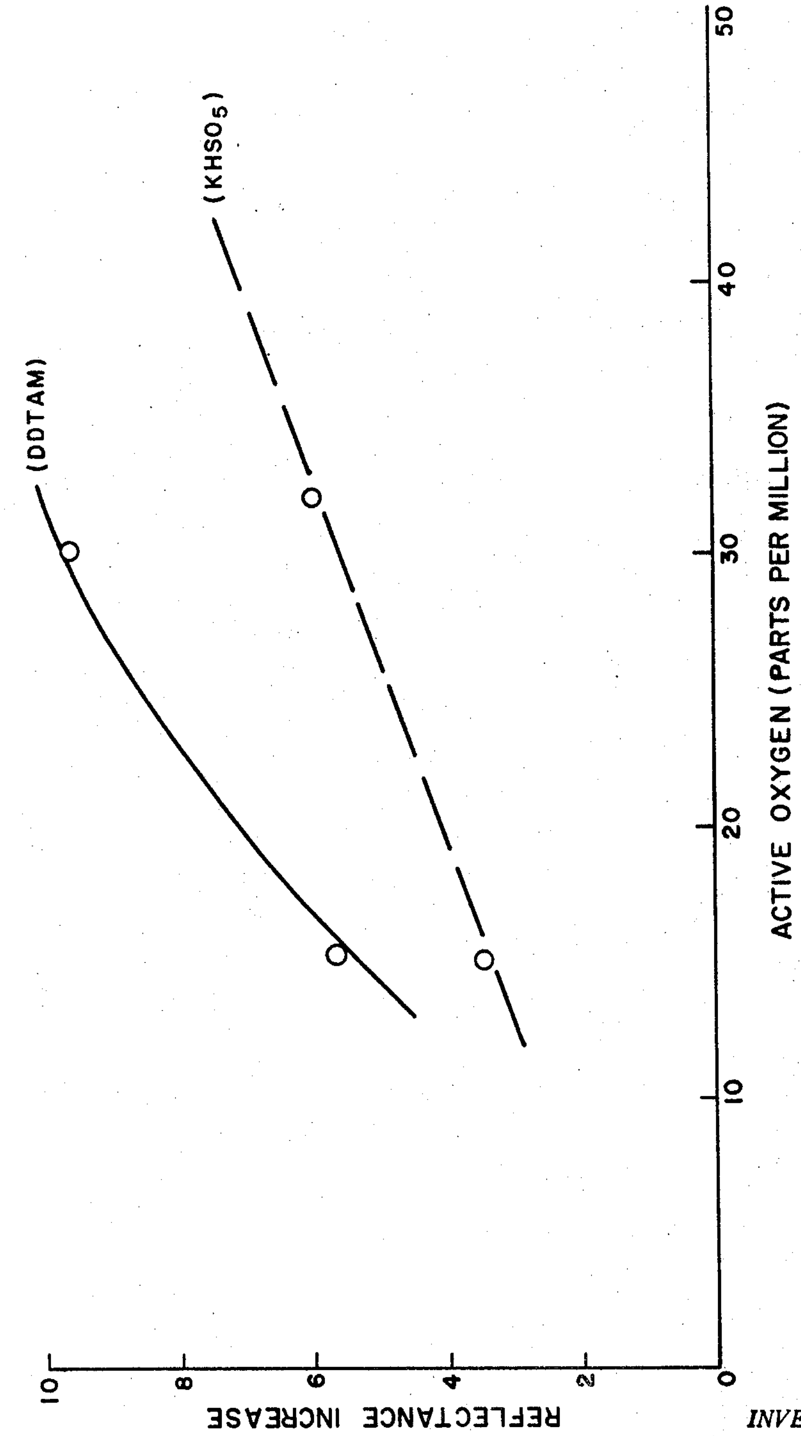
SEARCH RO

Nov. 21, 1967 L. H. DIAMOND ET AL **3,353,902**

METHOD OF USING QUATERNARY AMMONIUM PEROXYSULFATES

Filed May 8, 1964



INVENTORS
LOUIS H. DIAMOND
JOHN H. BLUMBERGS

BY Frank Ianno

Milton Zucker

United States Patent Office

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METHOD OF USING QUATERNARY AMMONIUM PEROXYSULFATES

Louis H. Diamond, Yardley, Pa., and John H. Blumbergs, Highland Park, N.J., assignors to FMC Corporation, New York, N.Y., a corporation of New York

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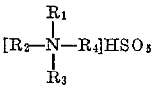
3 Claims. (Cl. 8—110)

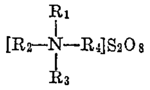
ABSTRACT OF THE DISCLOSURE

An improved class of bleaching agents has been found which is effective in giving a high degree of brightness without degrading fabrics during bleaching. These compounds are quaternary ammonium peroxysulfates having the formula:



$$\left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]HSO_5$$

and diquaternary ammonium peroxydisulfates having the formula:



$$\left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]_2S_2O_8$$

in which R_1, R_2, R_3 and R_4 may be saturated aliphatic, saturated cycloaliphatic or aromatic groups having up to 18 carbon atoms which are not oxidized by peroxysulfates and which are attached to the nitrogen atoms through a carbon atom.

In addition, certain of these compounds have also been found useful as fabric softeners, namely those quaternary ammonium compounds in which at least one of the alkyl groups has from about 12 to about 18 carbon atoms.

The present invention relates to an improved class of bleaching agents, and more particularly, to quaternary ammonium peroxymonosulfates and diquaternary ammonium peroxydisulfates (hereinafter termed peroxysulfates).

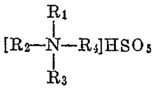
In the process of laundering textile garments in domestic washing machines, it is common to employ a bleaching agent in addition to a detergent to maintain the original whiteness of the garments after laundering. The bleaching agents which are commonly in use include such compounds as sodium hypochlorite, chlorinated isocyanuric acids, and potassium persulfate.

These bleaching agents have been found to have certain drawbacks. For example, sodium hypochlorite and chlorinated isocyanuric acids tend to cause a measurable amount of fabric degradation during bleaching and are capable of causing localized overbleaching by direct contact of the bleach with the fabric. Bleaching with potassium monopersulfate reduces fabric degradation, but the bleaching action is inferior to sodium hypochlorite. Further, potassium monopersulfate does not have a good shelf life and thus loses its bleaching effectiveness upon extended storage.

As a result, there is a need for an effective bleaching agent that is more active than the milder bleaching agents in common use but which does not cause any measurable degradation of the fabric during the bleaching operation.

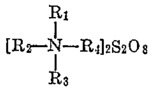
It is an object of the present invention to provide an active, stable, bleaching agent which is effective in giving a high degree of brightness without degrading the fabric during bleaching.

We have now found that quaternary ammonium peroxymonosulfates having the formula



$$\left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]HSO_5$$

and diquaternary ammonium peroxydisulfates having the formula

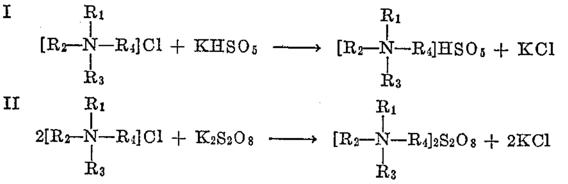


$$\left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]_2S_2O_8$$

are effective bleaching agents for bleaching fabrics and have good storage stability. In the above formulations, R_1, R_2, R_3 and R_4 may be saturated aliphatic, saturated cycloaliphatic or aromatic groups having up to about 18 carbon atoms which are not oxidized by peroxysulfates and which are attached to the nitrogen atom through a carbon atom. The aliphatic groups may be straight chained, branch chained, or attached to form a heterocyclic group.

We have further found that certain of these quaternary ammonium compounds are effective as fabric softeners as well as bleaching agents and can be employed for softening textiles while bleaching. The quaternary ammonium compounds useful for this purpose are those having only saturated alkyl chains on the quaternary ammonium residue and in which at least one of the alkyl groups has from about 12 to about 18 carbon atoms in the chain.

In accordance with the present invention, the quaternary ammonium peroxymonosulfates and the diquaternary ammonium peroxydisulfates are produced by reaction of a quaternary ammonium salt (preferably one in which the anion of the salt is a halogen element) and an inorganic mono- or dipersulfate. Typical reactions proceed according to the following equations:



$$\text{I}\quad \left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]Cl + KHSO_5 \longrightarrow \left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]HSO_5 + KCl$$

$$\text{II}\quad 2\left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]Cl + K_2S_2O_8 \longrightarrow \left[R_2-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}-R_4\right]_2S_2O_8 + 2KCl$$

where R_1, R_2, R_3, and R_4 are saturated aliphatic, saturated cycloaliphatic, or aromatic groups having up to about 18 carbon atoms which are not oxidized by peroxysulfates and which are attached to the nitrogen atom through a carbon atom. An alternate method for preparing monopersulfates is carried out by reacting quaternary ammonium hydroxides with Caro's acid solutions.

The particular quaternary ammonium salt precursor which is chosen will depend upon the requirements of the final quaternary ammonium persulfate. For example, if the final product is to be used for both softening and bleaching of textiles or in detergent applications, a quaternary ammonium salt having all alkyl groups, at least one of which is a fatty alkyl group, is prefered. Examples of these are dodecyl trimethyl ammonium chloride, di-hydrogenated tallow dimethyl quaternary ammonium chloride, and others. If the final product is to be used only for bleaching, lower molecular weight quaternary ammonium salt precursors can also be used with good effect such as tetramethyl ammonium chloride or tetraethyl ammonium chloride.

Most inorganic persulfate reagents can be used in making up the quaternary ammonium persulfates, but for economic reasons, the commonly available persulfates, e.g. the ammonium, potassium and sodium monopersulfates and dipersulfates, are preferred. For example, in the preparation of quaternary ammonium monoperoxysulfates, potassium monopersulfate (potassium caroate) has been found most suitable.

In the preparation of the quaternary ammonium peroxymonosulfates, low reaction temperatures should be employed, preferably not above 20° C. Low temperatures are required because these compounds have such a high activity that they will react at higher temperatures with the salt which is produced in situ to liberate free chlorine, and to convert the persulfate compound to a sulfate. Preferred reaction temperatures are from about zero to about 20° C.

In the production of the diquaternary ammonium peroxydisulfates, reaction temperatures of zero to 20° C. are preferred but either higher or lower reaction temperatures can be employed since the diquaternary ammonium peroxydisulfates do not react with any of the salts formed in situ. Lower temperatures are preferred but only to prevent the final product from being soluble in the reaction medium. At low temperatures, i.e. 0 to 20° C., the final product will crystallize from the reaction medium with a minimum of the product remaining soluble in the mother liquor. The use of temperatures substantially below 0° C. should also be avoided because, at these lower temperatures, some of the starting material may crystallize out of solution without being reacted and therefore will contaminate the final product.

The reaction media employed depends, to large extent, upon the solubility of the final product in the reaction media. It is chosen so that the final product is relatively insoluble in the reaction media while the precursor feed reactants remain soluble therein. For example, in the preparation of higher molecular weight, quaternary ammonium peroxymonosulfates and diquaternary ammonium peroxydisulfates, water is preferred because the final product is relatively insoluble in an aqueous reaction media whereas the feed reactants and the byproduct salt are sufficiently soluble to dissolve them in the reaction media. In the case of lower molecular weight quaternary ammonium peroxymonosulfates and diquaternary ammonium peroxydisulfates, a selective organic solvent media is preferred because the final product has a high solubility in water and recovery of the final product from a water medium would be extremely difficult. Suitable organic reaction media include aqueous methanol, dimethyl formamide, mixtures thereof, and isopropyl alcohol-aqueous mixtures.

The peroxysulfates which are suitable as bleaching agents in the present invention are those which have groups attached to the nitrogen atom that are not oxidizable by any peroxysulfate, including both monoperoxysulfates and diperoxysulfates. These groups, which are attached to the nitrogen atom through a carbon atom, may be saturated aliphatic, saturated cycloaliphatic, or aromatic groups. The aliphatic and cycloaliphatic groups must be saturated in order to be non-reactive with a peroxysulfate. The aliphatic and cycloaliphatic groups may be unsubstituted or may contain substituents that are nonoxidizable by peroxysulfates. Examples of aliphatic or cycloaliphatic substituents that are nonoxidizable include carboxyl, alkoxy, ester, amido and nitro groups. The aliphatic groups may also have phenyl substituents which are nonoxidizable and which conform to the requirements of aromatic groups set forth below. Substituents which can be oxidized on an aliphatic or cycloaliphatic group and which therefore are unacceptable include amino, hydroxyl, cyano, keto, halogens (except fluorine) and aldehydes.

In the case of aromatic groups, e.g. phenyl groups attached to the nitrogen atom, those may be unsubstituted or contain substituents such as carboxyl, alkoxy, ester, amide, nitro and halogen groups. The aromatic group may also have aliphatic substituents which are nonoxidizable and which conform to the requirements of aliphatic groups given above. Substituents which can be oxidized on an aromatic group and which therefore are unacceptable include amino, hydroxyl, keto, and aldehydes.

Examples of suitable peroxysulfates include quaternary ammonium monoperoxysulfates such as

2-ethyl lauryltrimethyl monoperoxysulfate,
2-ethyllauryl stearyl dimethyl monoperoxysulfate,
12-benzylstearyl trimethyl monoperoxysulfate,
2-phenylpalmityl lauryl dimethyl monoperoxysulfate,
10-m-chlorophenylstearyl trimethyl monoperoxysulfate,
2-nitrostearyl trimethyl monoperoxysulfate,
2-methoxystearyl lauryl dimethyl monoperoxysulfate,
10-cyclohexylstearyl ethyl dimethyl monoperoxysulfate,
2-carboxypalmityl lauryl dimethyl monoperoxysulfate,
2-acetoxystearyl propyl dimethyl monoperoxysulfate,
di-2-nitrostearyl dimethyl monoperoxysulfate,
phenyl stearyl dimethyl monoperoxysulfate,
di-p-nitrophenyl dimethyl monoperoxysulfate, and
p-carboxyphenyl diethyl methyl monoperoxysulfate.

The effectiveness of one of these peroxysulfates, dimethyl di-hydrogenated tallow ammonium monoperoxysulfate (DDTAM), as a bleaching agent compared with a conventional bleaching agent, potassium monopersulfate, is illustrated in the attached drawing.

In the drawing, the increase in brightness of tea stained samples (reflectance increase) is plotted against the active oxygen content of the bleaching solutions used. As is evident from the drawing, the present bleaching agent is more effective in increasing the reflectance, and therefore, in brightening the sample than is ($KHSO_5$) potassium monopersulfate. The exact procedure employed in determining these results is given in Example 8.

The present class of peroxysulfates may be used in laundering solutions in amounts sufficient to supply up to about 30 parts per million of active oxygen based on the weight of the bleaching solution. Larger quantities may be used, but for economic considerations, larger amounts are undesirable; moreover, the bleaching effect is sufficient at this concentration to satisfy home laundering requirements. The precise quantities used depends upon the particular peroxysulfate chosen. For example, if a lower alkyl quaternary ammonium peroxysulfate is selected which is intended primarily as a bleaching agent without any fabric softening effect, it is added in amounts sufficient to supply about 30 parts per million of active oxygen. On the other hand, if a long chained quaternary ammonium peroxysulfate is employed to obtain a fabric softening effect, it can be added in amounts of about 0.1 to 0.15% on the weight of the fabric. When using low concentrations of these compounds to obtain fabric softening, the bleaching effect will not be as substantial as when higher concentrations of the quaternary ammonium persulfates are employed. However, even at low concentrations, the bleaching effect aids in maintaining the original whiteness of the fabric while giving a softening effect; this is important because subsequent yellowing of fabrics treated with chemical softeners often occurs due to chemical changes in the softener per se.

In utilizing the present reagents, the quaternary ammonium peroxymonosulfates are preferred because these reagents are more reactive and are stronger oxidizing agents than the diquaternary ammonium peroxydisulfates. In addition, the quaternary ammonium peroxymonosulfates have more active oxygen per molecular weight than the peroxydisulfates, and therefore, can be used in smaller amounts to obtain the same bleaching effect as is obtained with larger quantities of diquaternary ammonium peroxydisulfates.

The following examples are given to illustrate the invention and are not to be deemed limiting thereof.

Example 1

A charge of 7.56 grams of tetramethyl ammonium chloride dissolved in 75 grams of methanol was poured into a 250 ml. beaker. To the solution was added, with stirring, 6.85 g. of ammonium persulfate dissolved in 25 g. of dimethyl formamide. The reaction mixture was cooled to approximately 2 to 5° C. with an ice-water bath. An insoluble product crystallized from the reaction mixture and was separated from the mother liquor by filtration. The crude product was washed three times with 25 ml. each of cold methanol and was dried in a Rinco Evaporator under reduced pressure. A white crystal material was obtained weighing 9.5 g. It had an active oxygen content of 4.73% by weight as determined by iodometric titration. The crude product was purified by recrystallization from methanol and analyzed:

	Theory, percent	Found, percent
Carbon	28.22	28.26
Hydrogen	7.11	7.21
Nitrogen	8.23	8.32
Sulfur	18.84	18.06
Active Oxygen	4.70	4.73
Chlorine	None	None

The product was identified as tetramethyl ammonium diperoxysulfate.

Example 2

The same procedure used in Example 1 was repeated except that 14.5 grams of tetraethyl ammonium bromide was used instead of the tetramethyl ammonium chloride. A white crystalline product weighing 11 grams was recovered from the Rinco Evaporator. It had an active oxygen content of 3.49% by weight. The crude product was purified by recrystallization from methanol and analyzed:

	Theory, percent	Found, percent
Carbon	42.45	42.8
Hydrogen	8.91	8.86
Nitrogen	6.19	6.21
Sulfur	14.17	13.64
Active Oxygen	3.53	3.50
Bromine	None	None

The purified product was found to be essentially pure tetraethyl ammonium diperoxysulfate.

Example 3

An 11.5 g. sample of Arquad 12 was poured into a 250 ml. beaker and mixed with 2.16 g. of ammonium persulfate dissolved in about 10 ml. of water. Arquad 12 is a 50% solution of dodecyl-trimethyl ammonium chloride in aqueous isopropyl alcohol. No solid formation was observed in the reaction mixture at ambient temperatures. The mixture was then slowly added to a liter of cold water with vigorous agitation and white solids commenced to precipitate from the solution. The reaction mixture was then cooled to about 0° C. and the crystallized product was filtered from the mother liquor, washed twice with cold water, and dried on a Rinco Evaporator under reduced pressure. The product was a white solid weighing 5 grams and having an active oxygen content of 2.49% by weight. The product was purified by recrystallization from methylene chloride and analyzed:

	Theory, percent	Found, percent
Carbon	55.52	55.31
Hydrogen	10.56	10.41
Nitrogen	4.32	4.30
Sulfur	9.88	9.40
Active Oxygen	2.47	2.49

The product was identified as dodecyl-trimethyl ammonium diperoxysulfate.

Example 4

The same procedure used in Example 3 was repeated except that the reactants employed were 11.5 g. of Arquad 16 in place of Arquad 12 and 1.78 g. of ammonium persulfate. Arquad 16 is a 50% solution of palmityl-trimethyl ammonium chloride. The resultant product was a white solid weighing 5.6 g. and having an active oxygen content of 2.07% by weight. The product was recrystallized from methylene chloride and analyzed:

	Theory, percent	Found, percent
Carbon	59.96	59.61
Hydrogen	11.12	11.10
Nitrogen	3.68	3.66
Sulfur	8.42	8.03
Active Oxygen	2.10	2.07

The product was identified as palmityl-trimethyl ammonium diperoxysulfate.

Example 5

The procedure of Example 3 was repeated except that the reagents employed were 11.5 g. of Arquad 18 and 1.69 g. of ammonium persulfate. Arquad 18 is a 50% solution of stearyl-trimethyl ammonium chloride. A white solid product weighing 5.3 g. and having an active oxygen content of 1.93% by weight was obtained. It was identified as stearyl-trimethyl ammonium diperoxysulfate.

Example 6

The procedure of Example 3 was repeated except that the reagents employed were 5.75 g. of diisobutylphenoxyethyl dimethyl benzylammonium chloride (Hyamine 1622) and 1.21 g. of ammonium persulfite. A white solid product weighing 5.0 g. and having an active oxygen content of 1.73% by weight was obtained. It was identified as diisobutylphenoxyethyl dimethyl benzylammonium diperoxysulfate.

Example 7

A charge of 44 g. of Arquad 2HT was dissolved in a 150 ml. of methanol and poured into a 400 ml. beaker. Arquad 2HT is a proprietary composition containing 75% by weight of dimethyl di-hydrogenated tallow ammonium chloride. The fatty alkyl groups in this proprietary composition contain approximately 65% C_{18}, 30% C_{16} and 5% of C_{14} alkyl chains. The Arquad 2HT solution was cooled to 5° C. A solution made up of 15 g. of potassium monopersulfate (potassium caroate) assaying 88% dissolved in 150 ml. of distilled water was then added to the Arquad 2HT solution. The reaction mixture was stirred and further cooled to 0° C. A white solid product crystallized from the reaction mixture and was separated by filtration from the mother liquor. The resulting solids were washed twice with 100 ml. of a cold (—5° C.) methanol-water mixture and dried in a Rinco Evaporator under reduced pressure. The resultant white solid product weighed 36 g. and had an active oxygen content of 2.20% by weight. A sample of the product was purified by recrystallization from methylene chloride and analyzed:

	Theory, percent	Found, percent
Carbon	67.45	67.39
Nitrogen	2.16	2.16
Hydrogen	11.98	11.90
Sulfur	4.90	4.82
Active Oxygen	2.47	2.20

The resultant product was identified as dimethyl di-hydrogenated tallow ammonium monoperoxysulfate.

Example 8

The bleaching effect of dimethyl di-hydrogenated tallow ammonium monoperoxysulfate (DDTAM), produced by the method set forth in Example 7, was compared with a standard bleaching agent, potassium monopersulfate, using the following procedure: Thirty-two cotton swatches (5" x 5" desized cotton Indianhead fabric, uniform in weave and thread count) were stained with tea. The staining was accomplished by placing 5 tea bags in a liter of water and boiling for 5 minutes, and thereafter immersing the swatches in the tea and continuing the boiling for an additional 5 minutes. The stained swatches were than squeezed to remove excess fluid, dried, rinsed in cold water and dried.

Three of the stained cotton swatches were added to each of a series of stainless steel Terg-O-Tometer vessels (produced by the U.S. Testing Company) containing 1000 ml. of a 0.2% standard detergent solution at a temperature of 120° F. Measured amounts of each of the bleaches were then added to separate vessels sufficient to correspond to predetermined active oxygen contents. The pH of the solutions in the vessels were adjusted to 9.5 using soda ash. Cut-up pieces of white terry cloth toweling were added to provide a typical household wash water/cloth ratio of 20:1. The Terg-O-Tometer was then operated at 72 cycles per minute for 15 minutes at a temperature of 120° F. At the end of the wash cycle, the swatches were removed, rinsed under cold tap water and dried in a Proctor-Schwartz skein dryer. The tests were run in triplicate and include detergent blanks. Reflectance readings of the swatches were taken before and after the wash cycle with a Hunter Model D–40 Reflectometer using the blue filter. Each swatch was read twice (warp and fill) on either side, with a backing of 5 similarly soiled swatches. Fluorescent effect was excluded in all readings. The resultant reflectance increase over blank samples at various active oxygen concentrations is given in the drawing for both the DDTAM and the potassium peroxymonosulfate.

Example 9

The softening effect of dimethyl di-hydrogenated tallow ammonium monoperoxysulfate (DDTAM), produced by the method set forth in Example 7, was tested by the method set forth in ASTM D1175–55T. This test measures the number of standard flex abrasion cycles a cloth can withstand before being abraded. The test was carried out as follows: Cotton samples having thread counts of 80 x 80 and 136 x 64, and a Dacron sample were placed in a domestic washing machine and run through a domestic washing machine with a standard detergent. In the final rinse 4.72 grams of DDTAM (100% active material) were added to the 18 gallons of wash water. The total solids load was 7.5 pounds of (dry) cloth. This permitted the solution to deposit on the cloth 0.137% softener solids based on the weight of the cloth. A duplicate blank was also run in which no softener was added to the cloth. The samples thus treated were placed on the flex abrasion tester and the number of abrasion cycles was recorded before the cloth was abraded. The results of the tests are shown in Table I.

TABLE I

Sample Material	Abrasion Cycles	
	DDTAM	Blank
80 x 80 cotton cloth	681	241
136 x 64 cotton cloth	1,235	328
Dacron	10,149	8,134

Softening of the cloth is indicated by the increase in abrasion cycles required to abrade the cloth. Cloth which has been treated with a standard amount of a softener has increased flexibility and is more difficult to abrade. The greater the softener action, the greater the increase in abrasion cycles required.

Example 10

The procedure used in Example 7 was repeated except that the reagents used were 11.8 g. of Arquad 16 and 4.5 g. of potassium monopersulfate. Arquad 16 is a proprietary solution containing 50% by weight of palmityl-trimethyl ammonium chloride. The resultant solid product weighed 5.8 g. and had an active oxygen content of 3.05% by weight. It was identified as palmityl-as stearyl-trimethyl ammonium monoperoxysulfate.

Example 11

The procedure of Example 7 was repeated except that the reagents employed were 13.9 g. of Arquad 18 and 4.5 g. of potassium monopersulfate. The resultant white solid product weighed 5.8 g. and had an active oxygen content of 3.01% by weight. The product was identified as stearyl-trimethyl ammonium monoperoxysulfate.

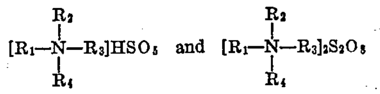
Example 12

The procedure of Example 7 was repeated except that the reagents employed were 23.5 g. of Aliquot 207 and 6.0 g. of potassium monopersulfate. The resultant white solid product weighed 20 g. and had an active oxygen content of 2.02% by weight. The product was identified as distearyl dimethyl ammonium monoperoxysulfate.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:

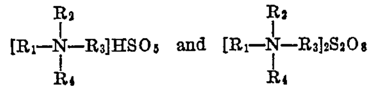
1. A method for bleaching fabrics which comprises contacting said fabrics with an effective amount of a bleaching agent selected from the group consisting of



$$[R_1-\overset{R_2}{\underset{R_4}{N}}-R_3]HSO_5 \quad \text{and} \quad [R_1-\overset{R_2}{\underset{R_4}{N}}-R_3]_2S_2O_8$$

in which R_1, R_2, R_3 and R_4 are selected from the class consisting of saturated aliphatic, saturated cycloaliphatic, and phenyl groups having up to about 18 carbon atoms, said groups not being oxidized by peroxysulfates and being attached to the nitrogen atom through a carbon atom.

2. A method for softening fabrics which comprises contacting said fabric with an aqueous dispersion of a compound selected from the group consisting of



$$[R_1-\overset{R_2}{\underset{R_4}{N}}-R_3]HSO_5 \quad \text{and} \quad [R_1-\overset{R_2}{\underset{R_4}{N}}-R_3]_2S_2O_8$$

in which R_1, R_2, R_3 and R_4 are alkyl groups having up to about 18 carbon atoms, and in which at least one of said alkyl groups has from about 12 to 18 carbon atoms.

3. Method of claim 2 in which the softening agent is dimethyl di-hydrogenated tallow ammonium monoperoxysulfate.

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LEON D. ROSDOL, *Primary Examiner.*

MAYER WEINBLATT, *Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,353,902 November 21, 1967

Louis H. Diamond et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 60, for "prefered" read -- preferred --; column 3, line 28, for "to" read -- to a --; line 68, for "those" read -- these --; column 4, line 4, for "2-ethyl lauryltrimethyl" read -- 2-ethyllauryl trimethyl --; column 8, line 4, before "solid" insert -- white --; same line 4, for "5.8 g." read -- 5 g. --; line 6, strike out "as stearyl-".

Signed and sealed this 24th day of June 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents